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Research Article

UTILIZATION OF WASTE COOKING OIL INTO BIODIESEL OVER HETEROGENEOUS SOLID ACID CATALYST

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ABSTRACT

The purpose of this investigation is to manufacture biodiesel from second-generation feedstock as waste cooking oil (WCO) by transesterification technique over a heterogeneous mesoporous solid acid catalyst. The $AlPO_4$ and $AlSiO_4$ catalysts were produced using a simple approach and calcined at 450°C before being characterized using SEM and HR-TEM. The images of SEM and HR-TEM exhibited crystalline and porous morphology. Waste cooking oil could be a feasible alternative to pure vegetable oil for biodiesel synthesis due to its low cost and absence of disposal difficulties. To enhance biodiesel yield, process factors such as temperature, ethanol: oil ratio, and catalyst dosage were changed to achieve optimization. The high conversion of WCO into biodiesel was obtained at room temperature with 1:3 ethanol: oil ratio, and 0.5 g catalyst dosage. The biodiesel conversion and selectivity of $AlPO_4$ and $AlSiO_4$ were tested by LC-MS analysis. The resultant products are characterized by FTIR and Mass spectrometry. This confirms and verifies the production of biodiesel. This study found that waste cooking oil will be utilized as a possible raw material for biofuel production after examining the experimentally produced biodiesel.

Keywords: Biodiesel, Optimization, Room temperature, Solid acid catalyst, Transesterification, Waste cooking oil.

1. INTRODUCTION

Recently, significant efforts have been made to identify renewable energy sources as alternatives to fossil fuels. Fossil fuel consumption has several public health and environmental dangers and has widespread and potentially irreversible effects on global warming [1, 2]. Biodiesel is a biofuel manufactured from vegetable oil or animal lipids that are based on alcohol [3]. Biodiesel can be produced from various edible feedstocks as sunflower, rapeseed, palm, soybean and castor oil using various catalysts [4]. But edible oil or pure vegetable oil is highly expensive and it increases the production cost of biodiesel. So there was a new route taken to synthesize biodiesel from non-edible feedstocks and it is a promising biofuel alternative. This process is highly economic, environmental, and gives a solution to waste management also. The term "waste cooking oil" (WCO) refers to the oil leftover from restaurants and food processing plants. In any country, the disposal of WCOs and fats is becoming a concern [5]. Homogeneous or heterogeneous catalysts have recently established much interest for their use in biodiesel production [6, 7]. But homogeneous catalysts used in biodiesel synthesis have some limitations; time-consuming process, poor product consistency, corrosiveness, toxicity, washing product, loss of biodiesel, large glycerol discharge, hazardous glycerol separation procedure, non-reusability, and doubling the cost of production [1,8-10]. Furthermore, heterogeneous catalysts can lower production costs and make products more affordable. This is because product separation is simpler with heterogeneous catalysts and it can be reused. So the demand for heterogeneous catalysts has increased. $AlPO_4$ and $AlSiO_4$ are more acidic and non-corrosive than homogeneous catalysts, are can be manufactured at a lesser cost, and are easier to handle. It was an interesting choice for a heterogeneous catalyst because it was eco-friendly in addition to these benefits. Biodiesel has been produced from waste vegetable oil using a variety of processes, including base-catalyzed transesterification, acid-catalyzed transesterification, enzyme catalysts, supercritical transesterification, and pyrolysis [11]. Biodiesel production can be done in a variety of reactors (e.g. batch, rotational packed-bed reactor, continuous flow, oscillatory flow, microwave reactor, supercritical) and with a variety of catalysts, as detailed in relevant papers [5,12]. Previously, various heterogeneous solid

base catalysts were synthesized to produce biodiesel from WCO, including KOH [11,13,14], KOH and NaOH [5], CaO nanocatalyst [1,4], amberlyst [15], Al-Fe_2O_3 [16]. Even though this catalyzed reaction produces a high yield of biodiesel parallelly it undergoes soap formation. So it needs a neutralization step. In addition to that these catalysts are necessitated high temperatures (45-60°C), high oil alcohol mole ratio (1:6 - 1:12) and catalyst dosage (0.7 wt% - 10.67). This process and technology present certain limits such as high reaction temperature, oil: alcohol ratio, low capacity, product quality issues, etc. As a result, its production and operation costs are high, which in turn indicates the need for the application of new technologies in biodiesel production. To overcome the issue, the heterogeneous solid acid catalysts are introduced in the transesterification reaction and it is the most cost-effective and simple process. The contribution of this study is important because of economic and environmental reasons and biodiesel could be one of the solutions. The primary goal of this research is to improve biodiesel synthesis from WCO feedstock to reducing reaction temperature, oil: alcohol ratio, and catalyst dosage with the help of $AlPO_4$ and $AlSiO_4$ catalysts. It prevents soap formation and corrosion also. These heterogeneous solid acid catalysts are necessary to maximize biodiesel yield at a low cost at the laboratory scale.

2. MATERIAL AND METHODS

Waste cooking oil was collected from cafes, restaurants, and street food vendors. The solid particle was filtered out of the WCO, which was then used as feedstock. Other chemicals used for the catalyst synthesis and ethanol (purity 99.8%), were utilized directly from Merck.

2.1. Synthesis of Catalyst

In a typical $AlSiO_4$ synthesis, cyclohexylamine (CA) is added to the aluminium chloride solution with continuous stirring. Then tetraethyl orthosilicate is added to the mixture slowly with vigorous stirring for 2 hours in a magnetic stirrer. The resultant product is washed repeatedly and filtered off and then dried in an oven at 120°C for 6 hours. The dried catalysts are calcinated at 450°C for 3 h. The same synthesis procedure is used for $AlPO_4$ also.

2.2. Liquid phase Transesterification Reaction

Biodiesel is a fatty acid monoalkyl ester generated from waste cooking oil, according to the chemical definition. WCO (triglyceride) is converted to biodiesel using a transesterification reaction with a sufficient catalyst.

Transesterification was executed in 100 ml two neck RB flasks connected with a water-cooled reflux condenser, oil bath, and magnetic stirrer. In a transesterification reaction, 10 ml of WCO was combined with a preferred molar concentration of ethanol and required gram of catalyst and stirred at the desired temperature with constant speed. Therefore, in this study, the biodiesel preparation reactions were performed on waste cooking oil: ethanol molar ratio (1:1, 1:2, 1:3, 1:4), reaction temperature (36, 50, 60 and 70°C), and $AlPO_4$ and $AlSiO_4$ dosage (0.5, 0.1, 1.5 2.0 *wt* %). The results of (%) yield of biodiesel differ with varying reaction parameters. After the finishing point of reaction, the solid acid catalyst was detached from the mixture and the remaining filtrate is subjected to HPLC analysis to quantify the fatty acid monoalkyl ester (FAME). The identified FAME mass was verified by LC-MS analysis.

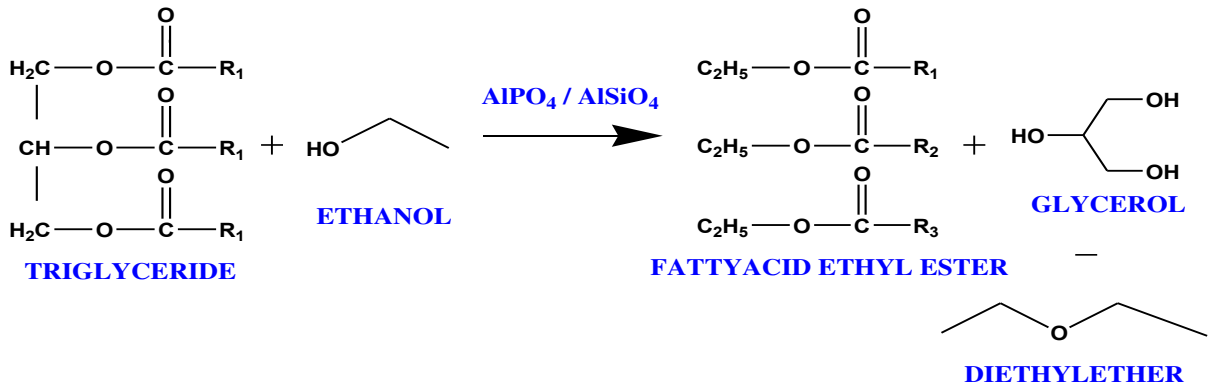


Fig. 1: Solid acid-catalyzed transesterification reaction using ethanol

3. RESULTS AND DISCUSSION

3.1. SEM-EDX and HR-TEM

The synthesized catalysts are characterized by SEM-EDAX and TEM analysis. The crystalline and porous morphology [17] was confirmed by SEM and HR-TEM (Figs. 2 a,b,d and e). Energy Dispersive X-ray (EDX) method was used to record the elemental contents of the synthesized samples $AlPO_4$ and $AlSiO_4$. The elemental contents based on EDX analysis results are revealed in Figs. 2c and 2f. Based on this result, it can be shown that $AlPO_4$ and $AlSiO_4$ samples consist of the elements that are used as precursors (Si, Al, P and O), while no other elements are detected. It indicated that there is no atomic impurity in the synthesized sample; all of the synthesized mesoporous $AlPO_4$ and $AlSiO_4$ have high purity.

The parameters like the effect of temperature, mole ratio and catalyst dosage are optimized for maximum conversion and selectivity over $AlPO_4$ and $AlSiO_4$.

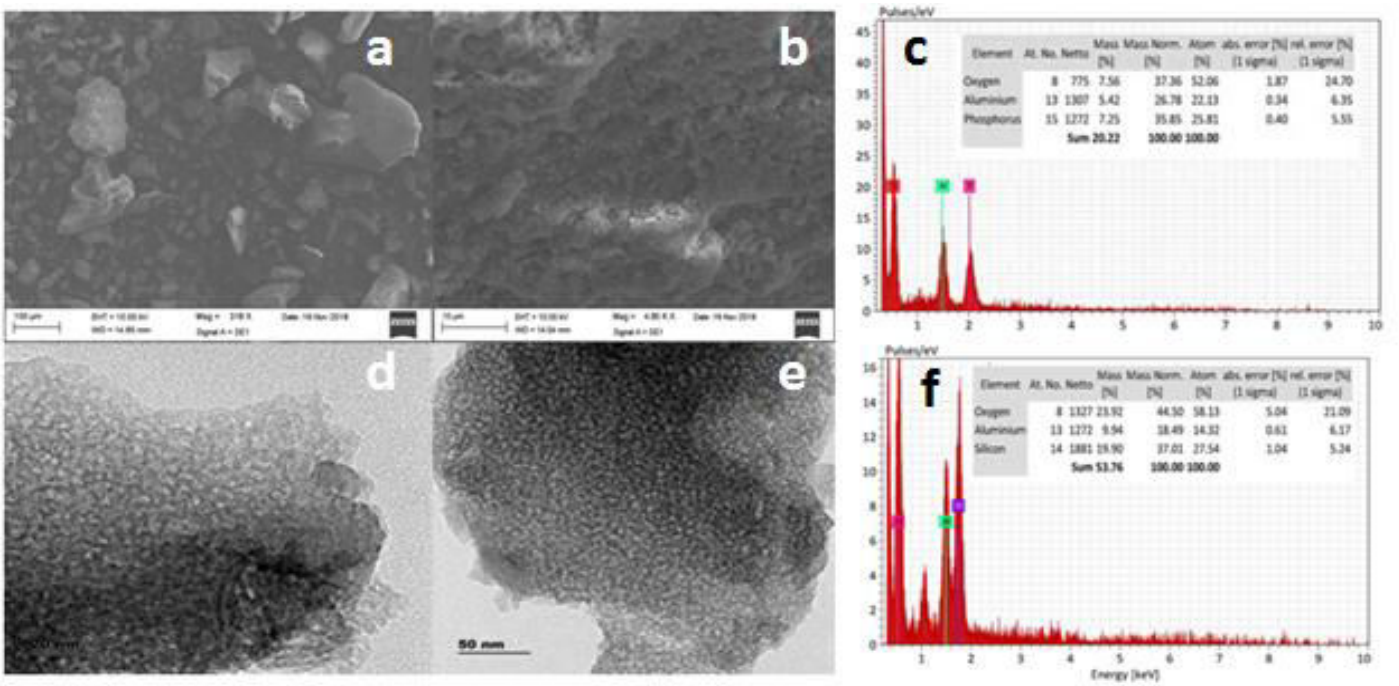


Fig. 2a and b: SEM images of $AlPO_4$ and $AlSiO_4$ c and d EDX and TEM images of $AlPO_4$ e and f TEM and EDX image of $AlSiO_4$

3.2. Effect of Temperature

Fig. 3 depicts the effect of reaction temperature on $AlPO_4$ and $AlSiO_4$ catalyzed transesterification of WCO. The transesterification was executed by varying the reaction temperature at 36-70°C to optimize the reaction temperature. The percentage of biodiesel increases at room temperature. By progressively increasing the temperature of both catalysts from 36 to 70°C, the conversion of biodiesel drops. A high conversion was attained at room temperature over $AlPO_4$ (26.4 %) and $AlSiO_4$ (39.7 %) respectively. Reported literature implies higher temperature is needed for biodiesel synthesis from WCO by using various catalysts [9,16]. But in this study room temperature is enough to produce biodiesel with a high yield.

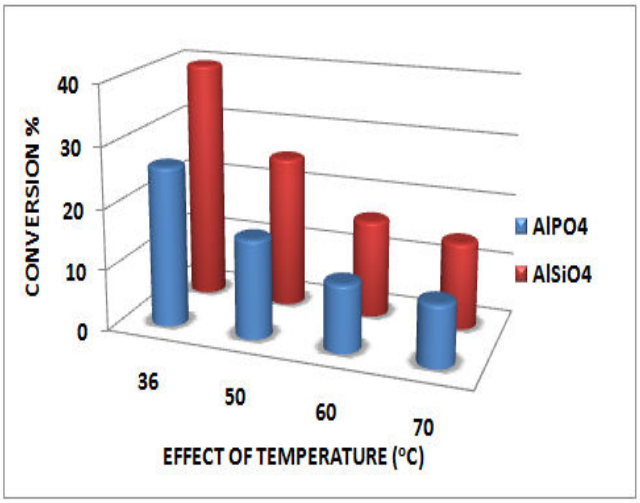


Fig. 3: Effect of temperature on $AlPO_4$ and $AlSiO_4$

3.3. Effect of Mole ratio

The Mole ratio effect of oil to ethanol is a significant parameter that affects not only the alkyl ester yield but also the biodiesel production cost. In this research, different oil to ethanol mole ratios like 1:1, 1:2, 1:3 and 1:4 was used. The output revealed that the conversion of biodiesel production increases with the increase of the mole ratio. The 1:3 mole ratio gave the higher conversion (39.6 % and 42.4 %) of biodiesel for $AlPO_4$ and $AlSiO_4$ catalysts than the 1:2 and 1:4 molar ratios (Fig. 4). In the reversible reaction, the excess of ethanol helped to change the equilibrium in the forward reaction so that it is possible to attain maximum ester yield in a relatively short time [18]. An Excess amount of alcohol enhances the transesterification rate and also displaces product molecules from the surface of the catalyst to recreate the active sites.

3.4. Effect of Catalyst Dosage

Catalyst concentration can influence biodiesel production. Fig.5 depicts the effect of catalyst dosage on the transesterification that has been performed at changing catalyst dosages from 0.5, 1.0, 1.5, 2 wt % for both the catalyst. It was observed that initially, (0.5 wt%) conversion of WCO into biodiesel increases the percentage of 29.3 and 42.4 of $AlPO_4$ and $AlSiO_4$ respectively. When the catalyst concentration increases, the conversion of biodiesel get decreases. So, 0.5 wt % is considered as an optimum parameter. The reaction optimum conditions were kept at oil: alcohol 1:3 mole ratio, room temperature. The percentage of conversion and selectivity was observed in fig. 5. This confirmed that 0.5 wt% catalyst dosage is sufficient to produce a greater yield of biodiesel.

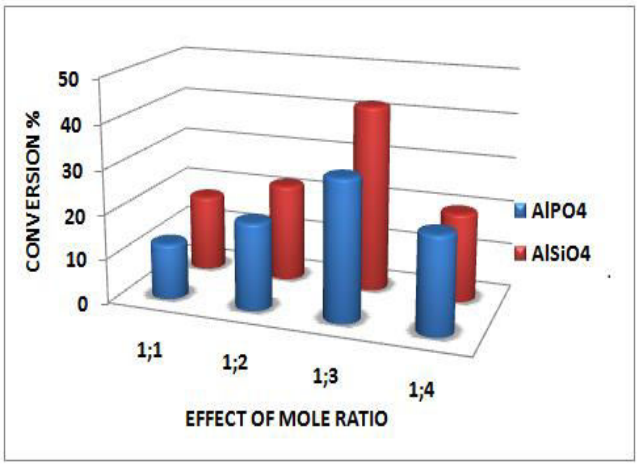


Fig. 4: Effect of mole ratio on $AlPO_4$ and $AlSiO_4$

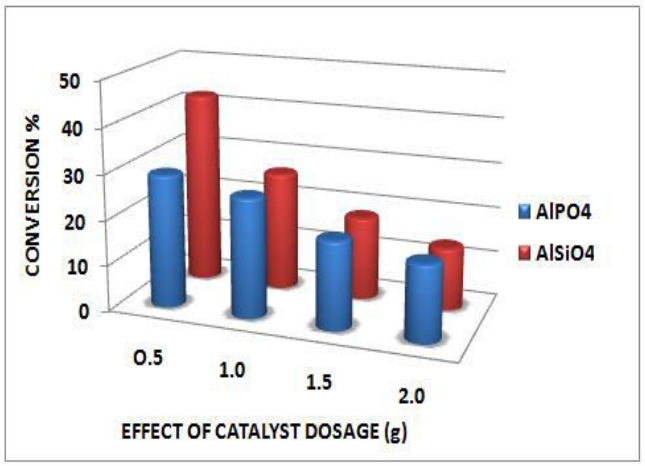


Fig. 5: Effect of catalyst dosage on $AlPO_4$ and $AlSiO_4$

Excessive catalyst dosage causes slurry viscosity to rise, resulting in unsatisfactory reaction mixtures [19]. This is the reason that an inadequate gram of catalysts results in a partial conversion of the WCO into the fatty acid esters.

3.5. Product Selectivity of Biodiesel

The catalytic activity of $AlPO_4$ and $AlSiO_4$ are verified by the transesterification reaction. In this reaction, different products obtained are biodiesel, glycerol and diethyl ether. Fig. 6 shows the biodiesel conversion and selectivity over $AlPO_4$ and $AlSiO_4$. The maximum yield of $AlPO_4$ and $AlSiO_4$ is 70.4 % and 91.6 % at optimum conditions like 0.5g catalyst, room temperature and1:3 mole ratio respectively. Few byproducts obtained in biodiesel productions are glycerol and diethyl ether. The determination of FAME quantification is validated by the HPLC method. The retention time comparison of the reference standard was used to determine the FAME peak identifier.

3.5.1. Product characterization of biodiesel

The biodiesel selectivity is varied with different parameters. The maximum biodiesel yield was attained with optimum parameters. FTIR and LC-MS were used to identify the biodiesel that resulted.

3.5.2. FTIR spectrum of Biodiesel

Biodiesels main components are aliphatic hydrocarbons, the chemical structures of which are identical to the long carbon side chains of biodiesel's main constituents. Fig. 7 shows the main characteristics peak of biodiesel occurs at 1726 -1695 cm^{-1} and corresponds to

triglyceride ester linkage. Furthermore, biodiesel is primarily monoalkyl ester, with the strong methyl ester stretching band C = O appearing at 1743 cm^{-1}[20]. The medium C -O bands at 1252, 1200, and 1175 cm^{-1} have also appeared in the FTIR spectrum. The absorbance at 1376 cm^{-1} indicated the stretching of the C-H bond. The FTIR spectrum results revealed that the biodiesel contained FAME and the functional group characteristics band of C = O, C-O, C-H bond [21].

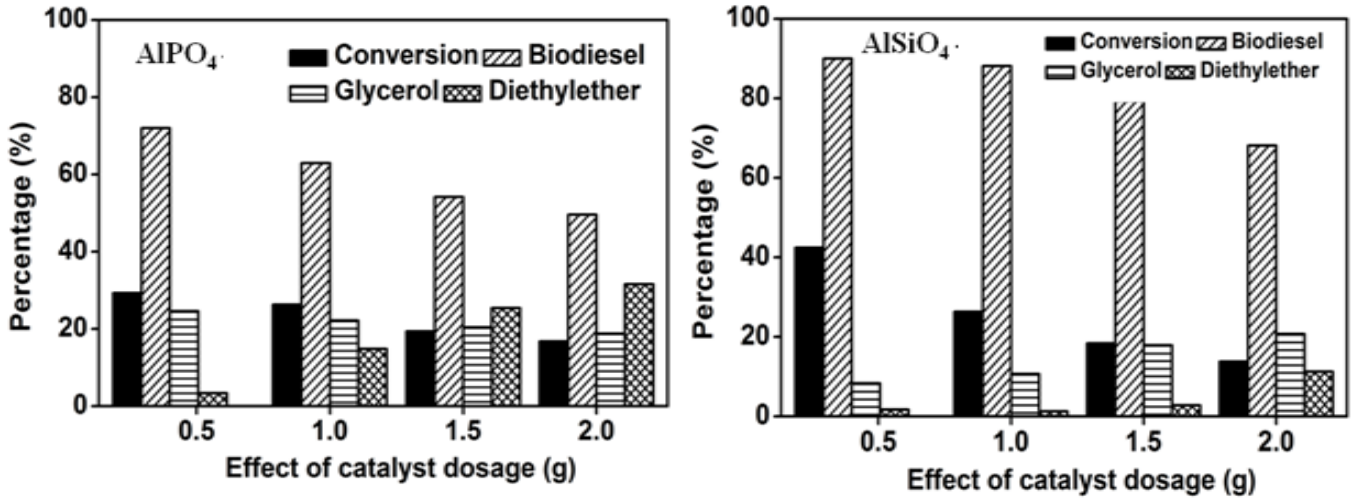


Fig. 6: Product selectivity of biodiesel $AlPO_4$ and $AlSiO_4$

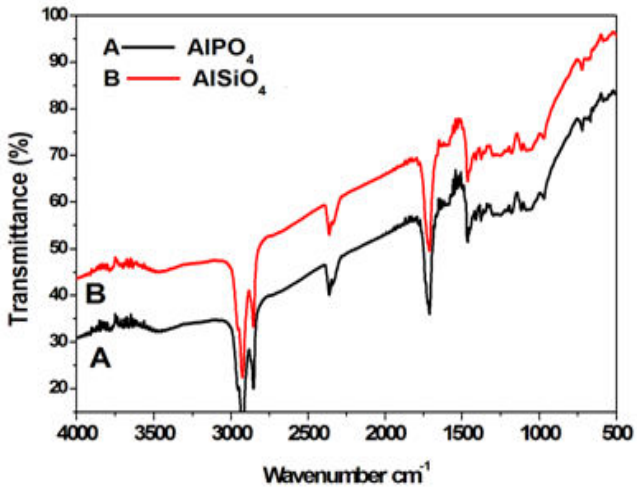


Fig. 7: FTIR spectrum of $AlPO_4$ and $AlSiO_4$

3.5.3. LC-MS analysis

Oils are typically natural products composed of triglyceride-derived ester mixtures, whose fatty acid chains contain around 14 to 20 carbon atoms with varying degrees of unsaturation. The transesterification reaction converts the triglyceride molecules by ethanol into corresponding fatty acid esters. Differences in the chemical composition of the waste cooking oil are represented by differences in the mole ratio of different fatty acids within the structure, according to the feedstock. Analysis of the LC-MS was conducted to determine the chemical fragmentation of ethyl ester (biodiesel). Ethyl ester is primarily formed through the transesterification of unsaturated and saturated fatty acids [22].

In the LC-MS biodiesel spectrum, three large peaks were observed above $AlPO_4$ and $AlSiO_4$ (Fig.8). Authentic FAME reference standards with mass spectral matching and corresponding retention time were used to annotate C14:0 (myristic acid ethyl ester; ethyl myristate), C16:0 (palmitic acid ethyl ester; ethyl palmitate), and C18:0 (oleic acid ethyl ester; ethyl oleate) [23, 24]. Fig. 8 Shows the signature FAME marker ions m/z 270, 284 and molecular ions m / z 324 for the mass spectral chromatogram. Other components that have very similar fragmentation patterns having characteristic peaks at m/z 83, 106,141,183 are diethyl ether, glycerol, C6:0 (capric acid ethyl ester; ethyl caproate) and C8:0 (caprylic acid ethyl ester; ethyl caprylate) respectively. Waste cooking oil contains various fatty acids. But it contains oleic acid (59.7) percentage is more. The chromatogram reveals a well-defined peak of C18:0 (Oleic acid ethyl ester; ethyl oleate). This is further confirmed the generation of biodiesel by mass spectrum.

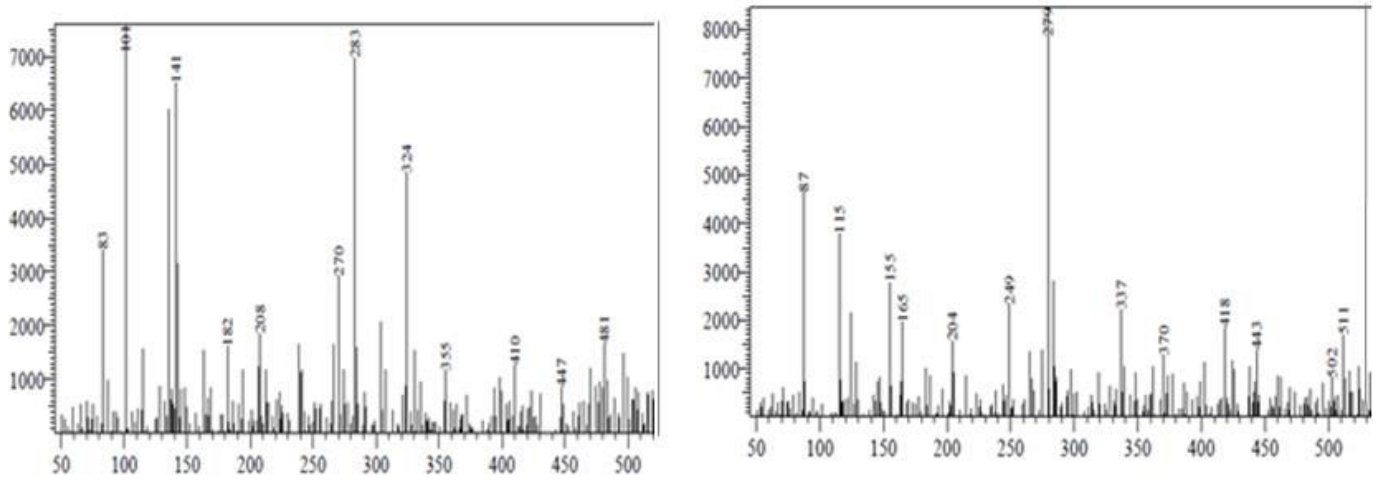


Fig. 8: Mass spectrum of biodiesel over $AlPO_4$ and $AlSiO_4$

4. CONCLUSION

To Summarize, a simple approach was developed for the synthesis of mesoporous $AlPO_4$ and $AlSiO_4$ materials using CA as a template. Both the materials exhibited good textural properties. These materials are suitable for catalytic application for the synthesis of biodiesel at room temperature. Both the catalysts are active for transesterification reaction at room temperature, mole ratio 1:3, and the catalyst dosage is 0.5g. The product selectivity of $AlSiO_4$ is 90.6 % higher than $AlPO_4$ (72 %). This difference may be due to the active sites present in the catalyst. FAME identity has been confirmed by analysis of mass spectrometry. The mass spectrum is a confirmation of biodiesel production. Although there are several reactions to oil conversion, these catalysts facilitated biodiesel production through transesterification reaction at room temperature. The current study will be useful for wide industrial applications.

Declaration of Interest

The author has no conflict of interest

5. ACKNOWLEDGEMENT

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